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Physics

Translated from Doklady Akademii Nauk SSSR, 91, 1059-62 (1953)

On the Theory of the Fine Structure of the X-Ray Absorption Spectra of Ions in Solutions

E. Ye. Vainshtein

It has recently been shown¹ that the method previously used^{2, 3} for analyzing the absorption edges of atoms in the molecules of a gas can be used to compute, in the first approximation, the structure of the x-ray absorption spectra of ions in solutions. It was assumed that the effect of the molecules of the solvent and the multiplet structure of the terms of ions cause an additional broadening of the selective absorption lines (in comparison with gas), and that the value of this broadening remains constant for all the lines of the series. For this reason, during the synthesis of the theoretical absorption curve, the shape of the first absorption line was established by the symmetrical reflection of the long-wave section of the experimental absorption edge, and the shape of the other lines of the series by the proportional decrease of the ordinates of the first of these lines. Such a method of constructing the lines of selective absorption and of the synthesis of the theoretical curve can, of course, be considered a doubly approximate method. The need for improving and refining this method has become especially evident in connection with the latest experimental investigations in this field.⁴ This paper describes a more precise method for calculating the structure of the x-ray absorption spectra of ions in solutions and reports certain results of the use of this method in analyzing the absorption edges of the ions Zn^{++} and Cu^{++} in various solvents.

It is well known^{2, 3, 5} that the shape of the lines of selective x-ray absorption of atoms in the molecules of gases, whatever the degree of their complexity, is well described by the dispersion formula.⁶ The width of such a line in the arbitrary cross section x_m , characterized by the quantity m (the ratio of the intensity I_0 of the line at the maximum to the intensity I on the contour at the level of the chosen cross section), is related⁷ to the so-called half-width Γ by the equation

$$\frac{x_m}{\Gamma} = \sqrt{m-1}. \quad (1)$$

The degree of consistency of the theoretical curve $x_m/\Gamma = f(m)$ with the experimental curve is illustrated by curve I in Fig. 1. The broken line represents the relation (1), and the crosses and points denote the experimental values of x_m/Γ for the first absorption line in the absorption edges of gaseous A and Ge in the molecule $GeCl_4$.

The situation is different for the x-ray absorption spectra of ions in solutions. In these spectra, the selective absorption lines are marked by

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their considerable width, and their shape is distorted in comparison with the dispersion shape. In the case of the ions Zn^{++} and Cu^{++} , for example, the relation between x_m/Γ and m can be represented by curve II in Fig. 1.

These peculiarities of the shape of the x-ray absorption lines of ions in solutions can be explained if we take into account the effect of the electric

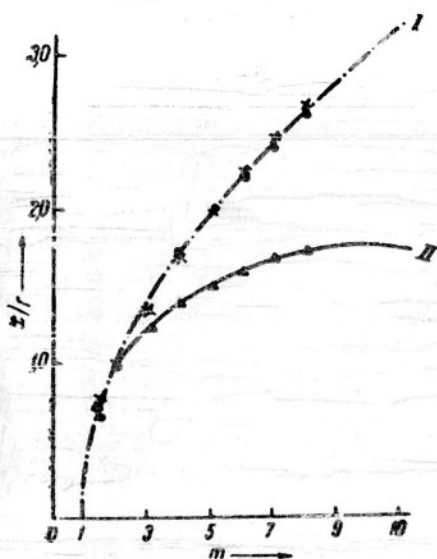


Fig. 1.

field of the molecules of the solvent, in which the ion in question is located, and the molecules of the solvate shell coordinated around the ion. The group of energy levels which capture the K -electron of the absorbing atom in the process of absorption is split under the action of the field; yet, because of the relatively small⁸ resolving power of the spectral instruments in the x-ray region, the group is perceived in toto as a wide absorption line (wider than that in gas), corresponding to a given value of the principal quantum number of the final level of the electron transition. At the same time, the interaction between the ion and the molecules of the solvent inside the solvate must produce a change in the polarizability of the solvated ion as compared with the free ion and, consequently,^{2, 3} a change in the energy range and structure of the

main absorption edge of this ion in various solvents. From this viewpoint, we begin to understand the results of recent experiments⁴ concerned with x-ray absorption spectra of ions in various solvents. For their theoretical interpretation we may limit ourselves to an examination of the linear Stark effect.⁹

For simplicity, we first make certain assumptions concerning the intensity of individual components. We may then assume that, because of the effect of the molecular field, the x-ray absorption lines that are narrow in a gas become, in a solution, a band whose width is determined by the distance between the extreme components of the term which is split as a result of the Stark effect. The well-known formula for this last quantity, which we shall denote by Δ , is

$$\Delta = \text{const.} \frac{n(n-1)}{\eta} \bar{F}, \quad (2)$$

where \bar{F} is the magnitude of the average electric field acting on the solvated ion in the solution,¹⁰ n is the principal quantum number, and η is the effective charge of the K -ionized solvated ion. In view of the above, we represent the total width of the selective absorption line in the absorption spectrum of the ion in solutions by

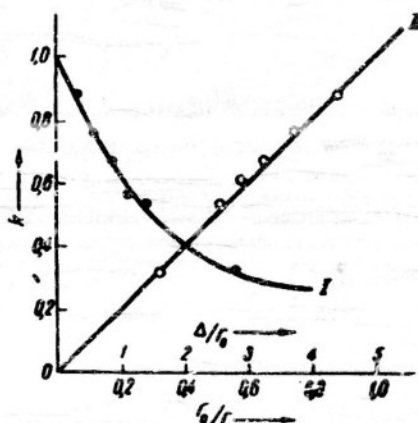


Fig. 2. I, dependence of k on Δ/Γ_0 ; II, dependence of k on Γ_0/Γ .

$$\Gamma = \Delta + k\Gamma_0, \quad (3)$$

where Γ is the experimentally observed width of the line in the absorption spectrum of an ion in the solution, Γ_0 is the width of the initial level of the transition (almost equal to the width of the corresponding absorption line in the x-ray spectrum of an atom in a gaseous molecule), and k is a coefficient varying from 0 to 1.

The value of this coefficient depends on the experimental ratio of Γ and Γ_0 ; its numerical value, corresponding to the value of the ratio Δ/Γ_0 or Γ_0/Γ can be determined to a first approximation from the graphs in Fig. 2. Eqs. (2) and (3) imply that, in contradistinction to the case of x-ray absorption spectra of molecules of gases, the value Γ for the ion spectra in solutions must increase with the increase of the principal quantum number, which characterizes the final level of the transition of the $1s$ -electron of the atom during absorption. In this case¹¹

$$\frac{\Delta_{n+1}}{\Delta_n} = \frac{n+1}{n-1},$$

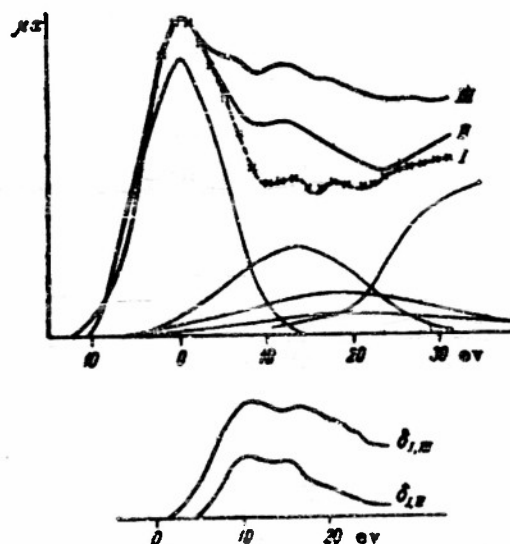


Fig. 4. X-ray absorption spectra for Zn in methyl alcohol. I theoretical total absorption curve, II experimental absorption curve for $\text{Zn}(\text{NO}_3)_2$, III experimental absorption curve for ZnCl_2 . The thin lines are the contours of the selective absorption lines; $\delta_{I, II}$ and $\delta_{I, III}$ are the differences between the curves I and II, and I and III, respectively.

same time, in comparing the theoretical absorption curve and the experimental curves obtained for the ion under study in a nonaqueous solvent in the

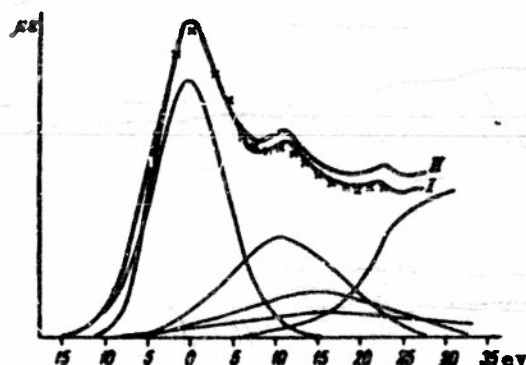


Fig. 3. X-ray absorption spectra for Zn in an aqueous solution. I, experimental absorption curve for $\text{Zn}(\text{NO}_3)_2$; II, experimental curve for ZnCl_2 . The thin lines are the contours of the selective absorption lines. The crosses are the points corresponding to the theoretical absorption curve.

and the quantity Γ for large values of n (corresponding to small values of the ratio Γ_0/Γ) becomes almost equal to Δ .

By the method described above for computing Γ for successive selective absorption lines in x-ray spectra of ions in solutions, we can reproduce the contours of these lines on the basis of the experimentally established relation $x/m = f(m)$ (Fig. 1, II), and construct the theoretical absorption curves according to the method of references 2 and 3. Some of the curves referring to the ion Zn^{++} in water and in methyl alcohol¹² are compared in Figs. 3 and 4 with experimentally obtained absorption edges.⁴ As the figures show, in all cases the trends of the theoretical and experimental absorption curves are quite similar, and in aqueous solutions these curves can be considered practically coincident. At the

presence of various anions (chloride-ion and an ion of NO_3^-), certain differences may be noted. It seems probable that the more complicated structure in the experimentally observed absorption edges than in the case of the theoretical curve is related to the presence of differently dissociated ions in the solutions. In this connection it is interesting to note that the difference curves $\delta = \delta(\nu)$ in Fig. 4 are quite similar in shape and differ only in intensity.

The foregoing conjecture is consistent with potentiometric and spectrophotometric studies of solutions.¹³ It also helps to explain the fact that the structure of the x-ray spectrum of the absorbing ion in the presence of a chloride ion is more complex than in the presence of an ion of NO_3^- .

¹Narbutt, Barinsky, and Vainshtein, Doklady Akad. Nauk SSSR, 82, 567 (1952).

²Vainshtein, Barinsky, and Narbutt, Doklady Akad. Nauk SSSR, 77, 1003 (1951).

³Vainshtein, Barinsky, and Narbutt, Doklady Akad. Nauk SSSR, 78, 39 (1951).

⁴E. Ye. Vainshtein and V. S. Kavetsky, Doklady Akad. Nauk SSSR, 91, No. 4 (1953) [translated in the present series as NSF-tr-141].

⁵Barinsky, Narbutt, and Vainshtein, Doklady Akad. Nauk SSSR, 79, 49 (1951).

⁶This is also the case for certain solids; see Vainshtein, Narbutt, and Barinsky, Doklady Akad. Nauk SSSR, 82, 701 (1952).

⁷E. Ye. Vainshtein, *Rentgenovskiy spektry atomov v molekulakh khimicheskikh soedinenii i v splavakh* [X-Ray Spectra of Atoms in Molecules of Chemical Compounds and in Alloys], 1951, p. 11.

⁸This is accounted for by the fact that the initial level of the electron transition is wider in the x-ray region than in the optical region.

⁹The validity of this approximation rests on: (a) the proved possibility of considering the process of x-ray absorption by the ions Zn^{++} and Cu^{++} in solution on the basis of the hydrogenlike model (Vainshtein, Barinsky, and Narbutt, Zhur. eksptl. i teort. fiz., issue 11 (1952)); and (b) the experimental fact⁴ that the energy $(\eta/n^2)^2$ depends linearly on the dipole moment of the molecules of the solvent. This dependence can be explained very easily on the basis of the assumption made.

¹⁰If the ion under study is surrounded by dipole molecules, then the intensity of the field F is proportional to the value of the dipole moment of the latter.

¹¹We note that the $1s-np$ lines of selective absorption are so wide when $n > 9$ that their effect on the fine structure of spectra is negligible.

¹²The method also made it possible to calculate the absorption spectra of Cu^{++} obtained⁴ in aqueous and nonaqueous solutions.

¹³A. K. Babko and V. S. Kodenskaya, Zhur. obshchei khim., 17, 1081 (1947).

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